FLUOROCARBON CONTAMINATION FROM THE DRILL ON THE MARS SCIENCE LABORATORY: POTENTIAL SCIENCE IMPACT ON DETECTING MARTIAN ORGANICS BY SAMPLE ANALYSIS AT MARS (SAM). J. L. Eigenbrode[1], A. McAdam[1], H. Franz[1], C. Freissinet[1], H. Bower[2], M. Floyd[1], P. Conrad[1], P. Mahaffy[1], J. Feldman[3], J. Hurowitz[3], J. Evans[3], M. Anderson[3], L. Jandura[3], K. Brown[3], C. Logan[3], S. Kuhn[3], R. Anderson[3], L. Beegle[3], D. Limonadi[3], R. Rainen[3], and J. Umland[3], [1]NASA Goddard Space Flight Center, Greenbelt, MD 20771, Jennifer.l.eigenbrode@nasa.gov, [2]University of Maryland and Universities Space Research Association, Center for Research and Exploration in Space Science and Technology, Greenbelt, MD 20771, [3]Jet Propulsion Laboratory, Pasadena, CA 91011.

Introduction: Polytetrafluoroethylene (PTFE or trade name: Teflon by Dupont Co.) has been detected in rocks drilled during terrestrial testing of the Mars Science Laboratory (MSL) drilling hardware. The PTFE in sediments is a wear product of the seals used in the Drill Bit Assemblies (DBAs). It is expected that the drill assembly on the MSL flight model will also shed Teflon particles into drilled samples. One of the primary goals of the Sample Analysis at Mars (SAM) instrument suite on MSL is to test for the presence of martian organics in samples. Complications introduced by the potential presence of PTFE in drilled samples to the SAM evolved gas analysis (EGA or pyrolysis-quadrupole mass spectrometry, pyr-QMS) and pyrolysis-gas chromatography mass spectrometry (Pyr-GCMS) experiments was investigated.

Teflon from the MSL drill assembly: MSL houses three drill bits. Each bit has diaphragm seals that contain the sample in the collection chamber of the DBA. The diaphragm seals are composed of Teflon with glass fibers and molybdenum disulfide. Most particles (~50%) shed from the diaphragm seals during drilling are removed by sieving of powdered samples to <150-micrometer particle size. A multitude of drilling tests on different drilling testbeds at the Jet Propulsion Laboratory (JPL) suggest that drilled samples sieved to <150 micrometers and delivered to SAM may have 0.1 to 10 parts-per-million (ppm) Teflon by mass from the diaphragm seal.

Methods: Samples of the diaphragm seal and DBA-drilled and sieved rock samples were pyrolyzed to at least 1000 °C under helium in commercial benchtop mass spectrometer (MS) instruments (Frontier Lab Pyrolyzer/Agilent 7890A GC/5975C inert XL MSD and CDS 5200/Thermo UltraGC/DSQII MS) modified for low-fidelity, SAM-like EGA and pyr-GCMS experiments, and the high-fidelity SAM breadboard for EGA experiments at NASA Goddard Space Flight Center (GSFC). In EGA, evolved gases are sniffed directly by the quadrupole mass spectrometer. Pyr-GCMS experiments were performed with and without a hydrocarbon trap to focus the organic analytes and using non-polar columns (RTX-CLP and RTX-5) similar to SAM's GC5 and GC2 columns.

Results: Direct pyr-GCMS analysis of the diaphragm seal yielded two groups of pyrolysis products: (1) low-molecular-weight (LMW) perfluoroalkenes that are very volatile and elute as a single complex mixture on non-polar GC columns at temperatures greater than -35 °C, and (2) high-molecular-weight (HMW) perfluoroalkenes that compose 6 or more homologous series of compounds that separate on the non-polar GC columns (Fig. 1). HMW components account for 0.34 wt% ±0.07 wt% of the total pyrolysis product.

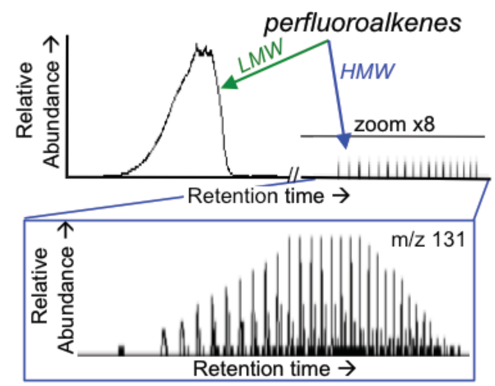

Figure 1. Pyr-GCMS results for the diaphragm seal. Total ion chromatogram (top plot) shows both low-molecular-weight (LMW) perfluoroalkenes eluting from the GC column (held at 35 °C in this example) during pyrolysis and significant lower abundances of high-molecular-weight (HMW) perfluoroalkenes that elute from the GC column during ramping to 300 °C. Ion chromatogram for m/z 131 (bottom plot) shows the 6+ homologous series that make up the HMW perfluoroalkene component.

Products have mass spectra consistent with the pyrolysis of the PTFE polymer (Fig. 2) [1], though no prior documentation of the HMW perfluoroalkene products were found in the literature. This HMW component is likely formed by incomplete pyrolysis of the PTFE polymer. All products are readily identified by a distinctive set of ions (see Fig. 2 caption).

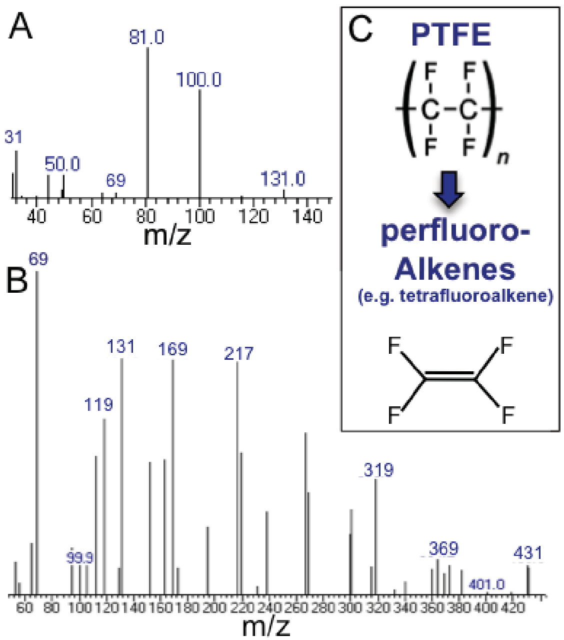

Figure 2. Mass spectrum of pyrolysate products of the diaphragm seal in the DBA. (A) Low molecular weight perfluoroalkene mixture including tetrafluoroethylene (most abundant product; m.w. = 100 amu) and probably hexafluoropropylene, octofluorocyclobutane, and octofluoroisobutylene [1]. (B) Example mass spectrum for one of the high molecular weight perfluoroalkene series. Key ion series for detection are M^++100n, where M^+ = 69, 119, 131, and 181. (C) The structure of PTFE, the primary component of the diaphragm seal in the drill, and its most abundant thermolysis product.

SAM breadboard EGA results for a basalt sample drilled at JPL show evolution of perfluoroalkene gases starting at 560 °C and continuing to higher temperatures. Breadboard results were corroborated by analyses on a commercial system that also showed a initial pyrolysis temp of 560 °C. LMW perfluoroalkenes compose the first peak, whereas larger perfluoroalkene products evolve at higher temperatures (Fig. 3).

Discussion: Pyrolysis products of the DBA diaphragm seal are mostly composed of a low-molecular weight perfluoroalkenes though traces of high molecular weight perfluoralkenes are also present. All pyrolysis products of the diaphragm seal were readily identified by SAM EGA and GCMS experiments based on mass spectra. Other suspect organic contaminants from the MSL drill to samples, such as Braycote lubricant and additives to the PTFE, were not definitively detected in EGA and GCMS experiments.

Conclusions: Parts-per-million quantities of total PTFE product will be several orders of magnitude greater than the SAM detection limit. Breadboard EGA experiments indicate that SAM will readily detect ppm

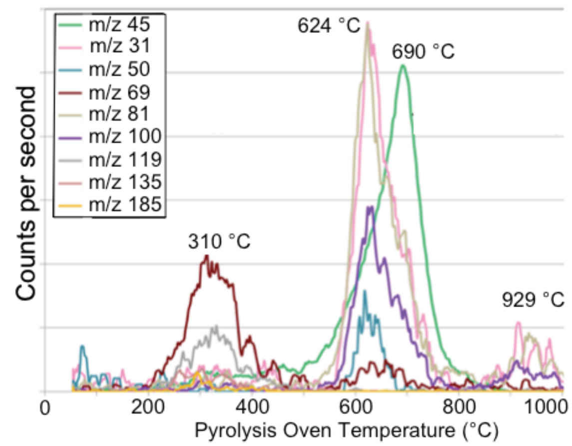

Figure 3. SAM breadboard evolved gas analysis results for 55 mg of Saddleback basalt rock drilled at JPL using the DBA and sieved to <150 micrometer particle size (sample tag: T28.1 G; analyzed May 2012). Low- and high-molecular-weight perfluoroalkenes evolve at 560-800 °C (max. at 624 °C) and above 800 °C (max at 924 °C), respectively. Other unresolved hydrocarbon components possibly derived from handling of the rock sample evolve at 200-500 °C. Y-axis for m/z 45 (CO_2) is scaled to 5% to fit the axis of other ions.

quantities of products from the diaphragm seal mixed in delivered samples. It is expected that the LMW perfluoroalkenes will be readily detected by the more sensitive GCMS experiment. GC co-elution of direct pyrolysis products (as shown here) may challenge interpretations and will be highly dependent on the samples organic and inorganic composition. Thermolytic reactions between pyrolysis products and other possible reactants in the oven, such as N-methyl-N-t-butyldimethylsilyl-trifluoro-acetamide (MTBSTFA) from SAM [2] or chlorate related compounds in rock samples [3], are under investigation. On Mars, characterization of PTFE products will be assessed by drilling the organic check material [4] (OCM; a control sample onboard the rover).

Perfluorocarbons are not found in nature, thus the PTFE pyrolysis products detected by EGA and pyr-GCMS experiments are not likely to be mistaken for martian organics if they are in samples analyzed by SAM. Further research is in progress to determine the science impact of PTFE products on isotopic measurements by the SAM QMS and tunable laser spectrometer (TLS).

References:

[1] Arito, H. and Soda, R. (1977) *Ann. Occup. Hyg. 20*, 247-255. [2] Sutter, B. (2013) *this meeting.* [3] Freissinet, C. et al. (2013) *this meeting.* [4] Conrad, P.G. et al., (2012) *Space Sci Reviews, 170,* 479–501.